

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

**EP 0 469 675 B1**

(12)

## EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention  
of the grant of the patent:  
08.05.1996 Bulletin 1996/19

(51) Int. Cl.<sup>6</sup>: **B01J 27/188**, B01J 35/10,  
C10G 45/08

(21) Application number: 91201947.8

(22) Date of filing: 25.07.1991

### (54) Hydrodesulphurization process

Verfahren zur hydrierende Entschwefelung

Procédé de hydrodésulphurization

(84) Designated Contracting States:  
AT BE DE DK ES FR GB GR IT NL SE

(30) Priority: 03.08.1990 NL 9001762

(43) Date of publication of application:  
05.02.1992 Bulletin 1992/06

(73) Proprietor: Akzo Nobel N.V.  
NL-6824 BM Arnhem (NL)

(72) Inventors:  
• Heijerman, Jacobus Johannes Leonardus  
NL-1077 PG Amsterdam (NL)  
• van Hengstum, Antonius Johannes  
NL-7421 GE Deventer (NL)  
• de Wind, Menno  
NL-1054 AB Amsterdam (NL)

(74) Representative: Schalkwijk, Pieter Cornelis et al  
AKZO NOBEL N.V.  
Patent Department (Dept. CO)  
P.O. Box 9300  
NL-6800 SB Arnhem (NL)

(56) References cited:  
EP-A- 0 164 162 EP-A- 0 244 106  
EP-A- 0 266 009 EP-A- 0 309 046  
US-A- 4 716 141 US-A- 4 941 964

#### Remarks:

The file contains technical information submitted  
after the application was filed and not included in this  
specification

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

**EP 0 469 675 B1**

## Description

The invention relates to a process for the catalytic hydrodesulphurization of hydrocarbon-containing feeds having a metals content of Ni plus V not exceeding 15 ppm and a boiling point range wherein more than 50 volume percent of the feed boils below 600 °C.

In general, the object of catalytically hydrotreating hydrocarbon-containing feeds is the complete or partial removal of impurities. Common impurities are sulphur compounds and nitrogen compounds. The at least partial removal of such impurities from a feed will ensure that, when the final product is burnt, fewer sulphur oxides and/or nitrogen oxides damaging to the environment will be released. In addition, sulphur compounds and nitrogen compounds are toxic to many of the catalysts employed in the oil industry for converting feeds into ready-for-use products. Examples of such catalysts include cracking catalysts, hydrocracking catalysts, and reforming catalysts. It is therefore customary for feeds to be subjected to a catalytic hydrotreatment prior to their being processed in, say, a cracking unit.

Catalytic hydrotreatment implies contacting a feed with hydrogen at elevated temperature and pressure in the presence of a hydrotreating catalyst. In this process the sulphur compounds and nitrogen compounds present in the feed are converted into readily removable hydrogen sulphide and ammonia.

In general, hydrotreating catalysts are composed of a carrier with deposited thereon a group VIB metal component and a group VIII metal component. The most commonly employed group VIB metals are molybdenum and tungsten, while cobalt and nickel are the conventional group VIII metals.

As a rule, such catalysts are prepared by impregnating a carrier with an aqueous solution of compounds of the metals in question, followed by a drying step and a calcination step. The impregnating solution will usually contain a phosphorus compound, such as phosphoric acid, to enhance the stability of the solution. See, *int. al.*, U.S. Patent Specification No. 3 840 472, in which it is recommended to dissolve first particular nickel salts or cobalt salts and then molybdenum trioxide in aqueous phosphoric acid, such that specific concentrations of the three components in the final solution are obtained. Over the years many different ways of improving the action of phosphorus-containing catalysts in hydrodesulphurizing processes have been proposed. See, *int. al.*, U.S. Patent Specification No. 4 392 985 and European Patent Specification Nos. 0 126 250 and 0 112 667.

US 4 392 985 describes that it is advantageous to keep the pH of the impregnating solution at a value of less than 1,2. EP-B 0 126 250 and EP-B 0 112 667 look to the use of catalysts having a specific, narrow pore size distribution to obtain the improvement, with EP-B 0 112 667 furthermore proposing that the use of a group VIII metal be dispensed with.

GB 2 055 602 describes catalysts having a comparatively high metals load, preference being given to nickel and molybdenum. The catalysts are prepared using a combination of multiple impregnating steps and a shaping step. This process is a highly specific one and inspired by the thought that "merely increasing the catalytic metals of any composition can eventually top out the activity effect and actually begin to give a decrease in activity at very high metals loadings."

US 4 444 905 describes a process for the preparation of a catalyst wherein an alumina or silica-alumina support is impregnated with a group VIB metal and a group VIII metal-containing solution, shaped, and subsequently calcined.

In US 4 014 821 a catalyst is described for the catalytic hydroconversion of hydrocarbon feeds having boiling points higher than 1050 °F (566 °C).

Although more or less acceptable desulphurization results can be obtained using the catalysts disclosed so far, there is permanent need for improved catalysts on account of the requirements as to the legally permitted sulphur content in fuels becoming ever stricter.

Equally, this need exists because at a given final sulphur content a more active catalyst will make it possible to operate under milder process conditions (energy saving) or to increase the life span of a catalyst prior to its needing regeneration (cycle length).

Furthermore, it is there because more and more additional demands are made on desulphurization catalysts with respect to their hydrodenitrogenation activity, their life cycle under mild hydrocracking conditions, and their capacity for producing the lowest possible olefin content in the end product (improving the colour, oxidation, and light stabilities).

The process according to the invention comprises contacting the above-mentioned hydrocarbon-containing feed, having a boiling point range at which more than 50 volume per cent of the feed boils below 600 °C under hydrodesulphurization conditions with a catalyst composition containing a porous, inorganic oxide carrier comprising transition alumina, a phosphorus component, a cobalt component, and a Group VIB metal component, wherein the phosphorus component content, calculated as  $P_2O_5$ , is 2 - 28 mmoles, the cobalt component, calculated as CoO, is 60 - 133 mmoles, and the Group VIB metal component content, calculated as trioxide, is 132 - 208 mmoles, all calculated on the basis of 100 grams of said catalyst composition, and said catalyst composition is prepared by a process in which a chemical precursor of the transition alumina is shaped, the shaped material is subjected to at least one calcining step in order to form transition alumina, and the precursors of the phosphorus component and the metal components are deposited on the carrier material prior to, during and/or after the shaping step, with the proviso that the cobalt component precursor is deposited after forming of the transition alumina.

The catalyst composition employed in the process according to the invention contains as carrier material a porous, inorganic oxide comprising transition alumina. These so-called transition phase aluminas (gamma, theta, delta aluminas)

may be used in combination with silica. Optimum results are obtained employing carriers containing at least 90 wt. % of transition alumina.

The phosphorus component content in the catalyst, calculated as  $P_2O_5$ , is 2-28 mmoles, preferably 2-21 mmoles, calculated on 100 g of catalyst composition. In percentages by weight these amounts come to 0,3-4,0 wt. % and 0,3-3,0 wt. %, respectively.

The cobalt component, calculated as  $CoO$ , is present in an amount of 60-133 mmoles, preferably 60-93 mmoles, calculated on 100 g of catalyst composition. In percentages by weight these amounts are 4,5-10,0 wt. % and 4,5-7,0 wt. %, respectively. Especially suited for use are catalysts containing 4,5-6,0 wt. % of cobalt component.

Preferred group VIB metals are molybdenum and tungsten, more particularly molybdenum. The group VIB metal component content, calculated as trioxide, is 132-208 mmoles, preferably 132-174 mmoles, calculated on 100 g of catalyst composition. For, say, molybdenum trioxide these amounts correspond to percentages by weight of 19,0-30,0 wt. % and 19,0-25,0 wt. %, respectively. Pre-eminently suited to be used are catalysts containing 19,0-23,0 wt. % of molybdenum trioxide.

For optimum results it is advisable that the ratio of the number of gram atoms of phosphorus to the sum of the number of gram atoms of cobalt and group VIB metal should be 0,020-0,25, preferably 0,020-0,20.

The catalyst should have a specific surface area of at least 100  $m^2/g$  (B.E.T. method) and a pore volume in the range of 0,25 to 1,3 ml/g (mercury penetration method; angle of contact  $140^\circ$ ). Preferably, the specific surface area is 150-300  $m^2/g$  and the pore volume is 0,30-1,0 ml/g. Also preferably, the catalyst has a monomodal pore size distribution.

The other pore characteristics of the catalyst may be selected as the feed to be treated requires. For many catalysts a suitable mode pore diameter will be in the range of 5-20 nm, preferably of 5-15 nm. The mode pore diameter (MPD) is defined as follows: 50% of the pore volume is in pores having a greater diameter than the MPD and the other 50% is in pores having a smaller diameter than the MPD. Preferred catalysts contain less than 5% of their pore volume in pores having a diameter of greater than 25 nm. Still more preferred catalysts contain less than 5% of their pore volume in pores having a diameter of greater than 20 nm. Especially in the case of feeds substantially made up of components having a boiling point of  $400^\circ C$  or lower preference is given to the use of catalysts of which at least 50% of the pore volume is in pores having a diameter in the range of 7-9 nm (mercury penetration method).

The catalyst is employed in the conventional manner in the form of spheres or extrudates. Examples of suitable types of extrudates have been disclosed in the literature (see, int. al., US 4 028 227). Highly suitable for use are cylindrical particles (which may be hollow or not) as well as symmetrical and asymmetrical polylobed particles (2, 3 or 4 lobes).

The preparation of catalysts to be employed in the process according to the invention may be carried out in several manners, using techniques known in themselves.

Suitable phosphorus component precursors include phosphoric acid and the various ammonium hydrogen phosphates. Suitable cobalt component precursors include cobalt nitrate and cobalt carbonate.

Suitable group VIB metal component precursors include ammonium dimolybdate and ammonium heptamolybdate. Also suitable for use are the trioxides of the group VIB metals, such as molybdenum trioxide.

These and other P-, cobalt-, or group VIB metal-containing compounds are known to the skilled man and will be referred to hereinafter as component precursors (this also applies to a compound such as molybdenum trioxide).

One suitable method of preparing a catalyst to be employed in the process according to the invention is by starting from the carrier in the pre-formed condition, such as an extrudate, using an aqueous solution of the component precursors in question to deposit thereon suitable amounts of said precursors, e.g. by means of impregnation, and then, after an optional drying step at a temperature in the range of  $25^\circ$ - $200^\circ C$ , calcining the resulting material at a temperature in the range of  $350^\circ$ - $750^\circ C$  to at any rate bring the phosphorus component and metal component precursors to the desired oxide form.

It will be clear to the skilled man that there can be a wide number of variations on this method. Thus, it is possible to apply a plurality of impregnating steps, the impregnating solutions to be used containing one or more of the component precursors that are to be deposited, or a portion thereof. Instead of impregnating techniques there can be used dipping methods, spraying methods, etc. With multiple impregnation, dipping, etc. drying and/or calcining may be carried out in between. Alternatively, one or more component precursors (other than the cobalt component precursor) can be mixed wholly or in part with the carrier prior to the shaping step being carried out. In such an embodiment the component precursor material, or a portion thereof, can be deposited on the not yet shaped carrier material, say, a powder, by means of, e.g., impregnation, after which the shaping step is carried out. Alternatively, it is possible to intimately mix one or more component precursors (other than the cobalt component precursor) wholly or in part with the carrier material during the shaping step rather than prior to it. Techniques that are suitable for this process are co-pelletisation and co-extrusion. It is recommended that the group VIB metal component precursor employed in this process be molybdenum trioxide.

Optimum results are obtained when care is taken to preclude any or virtually any reaction between the cobalt component precursor and the carrier material. Such a reaction will reduce the amount of cobalt that is effectively available for catalytic ends in the final catalyst. Notably when use is made of alumina-containing carriers the prospect of compounds or complexes containing cobalt and aluminium being formed is undesired. Such a reaction will occur when the cobalt component precursor is contacted with precursors of transition aluminas, such as boehmite, with subsequent

calcining to form the transition alumina. It is therefore essential to first subject the transition alumina precursor to a shaping step, e.g. extrusion, and to subject the resulting carrier to at least one calcining step, in order to obtain the transition alumina prior to the carrier being provided with the cobalt component precursor. During this calcination process, which is generally carried out at a temperature in the range of 400°-1000°C over a period of 0,5 to 16 hours in the presence of steam or not, the transition alumina precursor is converted into a transition alumina.

For an example of the preparation of a suitable alumina carrier, including the preparation of the transition alumina precursor (alpha-alumina monohydrate) reference is made to U.S. Patent Specification No. 4 154 812.

As indicated hereinbefore, to deposit the component precursors on the carriers use is generally made of one or more solutions of the component precursors in water. It has been found that the effectiveness of the final catalyst can be further enhanced still when the aqueous solutions also contain a compound selected from the group of nitric acid, formic acid, acetic acid, and polycarboxylic acids such as nitrilotriacetic acid, citric acid, and ethylene diamine tetracetic acid. Alternatively, salts and combinations of these compounds can be used. The appropriate amount is bound up with such factors as the nature of the component precursor(s) and the precursor concentration(s) and is simple to determine experimentally.

Like the prior art hydrodesulphurization catalysts the catalysts to be used in the process according to the invention are generally employed in the sulphided form. To this end use may be made of ex-situ as well as in-situ (pre)sulphidation techniques. Such methods are known to the skilled man.

The catalysts employed in the process according to the invention can be used to hydrodesulphurize a wide range of feeds. Examples of suitable feeds include middle distillates, kero, naphtha, vacuum gas oils, and heavy gas oils, more generally, hydrocarbon-containing feeds having a metals content (Ni + V) not exceeding 15 ppm, which feeds are substantially (> 50% by volume) composed of components having a boiling point below 600°C, preferably below 400°C.

The conventional process conditions, such as temperatures in the range of 250°-450°C, pressures in the range of 5-250 bar, space velocities in the range of 0,1-10 hr<sup>-1</sup>, and H<sub>2</sub>/oil ratios in the range of 50-2000 N/V, can be applied here. The presently used catalysts not only have an excellent desulphurization capacity, they can also effectively reduce the feed's olefin content (reduction of the bromine number), thus favourably affecting the obtained product's colour, light, and oxidation stabilities.

The invention will be illustrated with reference to the examples below.

#### Example 1

Preparation of a catalyst to be used in the process according to the invention.

First, an impregnating solution was prepared.

To 3 l of water of 40°C there were added successively, with stirring, 1,18 kg of cobalt carbonate and 0,45 kg of aqueous phosphoric acid (85%). The suspension had its temperature increased to and kept for 1 hour at 60°C, after which 2,74 kg of molybdenum trioxide were added. The temperature was then increased to and kept for two hours at 96°C, whereupon 476 g of aqueous nitric acid (65%) were added, after which a clear, stable, reddish-brown solution was obtained. The total volume of the solution was increased to 6,5 l by the addition of water, and then the solution was cooled to room temperature.

Next, 10 kg of  $\gamma$ -alumina (asymmetrical quadrulobe extrudates, 1,2 mm (short diameter) x 1,4 mm (long diameter); PV(H<sub>2</sub>O): 0,65 ml/g) were impregnated with the above-described solution. The impregnated material was allowed to age for 0,5 hours and then dried at 120°C, first for 1,5 hours in a rotating impregnator and then on a sheet for 24 hours. Finally, the dried material was calcined for 1,5 hours at 530°C in an air atmosphere.

The catalyst had a P<sub>2</sub>O<sub>5</sub> content of 2,0 wt.%, an MoO<sub>3</sub> content of 20,8 wt.%, and a CoO content of 5,1 wt.%. The pore volume was 0,41 ml/g (mercury penetration method), the surface area 207 m<sup>2</sup>/g, and the mode pore diameter 8,0 nm (mercury penetration method).

The Examples 2-11 below describe the preparation of four catalysts to be used in the process according to the invention (Examples 2-5) and six catalysts for comparative ends (Comparative examples 6-11).

Example 12 describes how the catalysts of Examples 1-11 were tested and also lists the results.

In preparing the present catalysts use was made of a carrier in the form of asymmetrical quadrulobe extrudates [1,2 mm (short diameter) x 1,4 mm (long diameter)] made up of 98,7 wt.% of  $\gamma$ -alumina and 0,7 wt.% of silica, having a surface area of 290 m<sup>2</sup>/g, and a pore structure such that the pore volume (Hg) in pores having a greater diameter than 4,2 nm was 0,58 ml/g and the mode pore diameter 6,7 nm (mercury penetration method).

All experimental procedures (preparing the impregnating solutions, the impregnations, dryings, and calcinations) were carried out as set down in Example 1, unless otherwise indicated.

#### Example 2

500 g of carrier were impregnated with 325 ml of an aqueous solution containing 137 g of molybdenum trioxide, 59,2 g of cobalt carbonate, 22,2 g of phosphoric acid (85%), and 34 g of nitric acid (65%). The impregnating solution

was prepared as described in Example 1, except that the order in which the molybdenum trioxide and the cobalt carbonate were added was reversed. The composition and properties of the catalyst obtained after drying and calcination were as listed in the table below.

#### 5 Example 3

350 g of carrier were impregnated with 230 ml of an aqueous solution containing 94 g of molybdenum trioxide, 40,6 g of cobalt carbonate, 3,8 g of phosphoric acid (85%), 29,4 g of nitric acid (65%), and 16 g of citric acid. The impregnating solution was prepared as described in Example 1, except that after the nitric acid citric acid was added.

10 The composition and properties of the catalyst obtained after drying and calcination were as listed in the table below.

#### Example 4

1500 g of carrier were impregnated with 1000 ml of an aqueous solution containing 405,3 g of molybdenum trioxide, 175,2 g of cobalt carbonate, 33 g of phosphoric acid (85%), and 142,8 g of nitric acid (65%). The composition and properties of the catalyst obtained after drying and calcination were as listed in the table below.

#### Example 5

20 1000 g of carrier were impregnated with 650 ml of an aqueous solution containing 352,9 g of molybdenum trioxide, 116,0 g of cobalt carbonate, 72,4 g of phosphoric acid (85%), and 35 g of nitric acid (65%). The composition and properties of the catalyst obtained after drying and calcination were as listed in the table below.

#### Comparative example 6

25 500 g of carrier were impregnated with 325 ml of an aqueous solution containing 120 g of molybdenum trioxide, 57,6 g of cobalt carbonate, 21,7 g of phosphoric acid (85%), and 25 g of nitric acid (65%). The composition and properties of the catalyst obtained after drying and calcination were as listed in the table below.

#### 30 Comparative example 7

500 g of carrier were impregnated with 325 ml of an aqueous solution containing 134,2 g of molybdenum trioxide, 45,3 g of cobalt carbonate, 33,9 g of phosphoric acid (85%), and 26 g of nitric acid (65%). The composition and properties of the catalyst obtained after drying and calcination were as listed in the table below.

35

#### Comparative example 8

500 g of carrier were first impregnated with 325 ml of an aqueous solution containing 104,7 g of ammonium dimolybdate (a solution obtained by simply dissolving the ammonium dimolybdate in water). The material obtained after drying and calcination (563,4 g) was impregnated with 325 ml of an aqueous solution containing 155,8 g of molybdenum trioxide, 66,9 g of cobalt carbonate, 25,2 g of phosphoric acid (85%), and 30 g of nitric acid (65%). The composition and properties of the catalyst obtained after drying and calcination were as listed in the table below.

#### 45 Comparative example 9

500 g of carrier were first impregnated with 325 ml of an aqueous solution containing 149,2 g of molybdenum trioxide, 64,5 g of cobalt carbonate, 24,1 g of phosphoric acid (85%), and 20 g of nitric acid (65%). The material obtained after drying and calcination (563,4 g) was subsequently impregnated with 325 ml of an aqueous solution containing 168,5 g of cobalt nitrate.6H<sub>2</sub>O (a solution obtained by simply dissolving the cobalt nitrate in water). The composition and properties of the catalyst obtained after drying and calcination were as listed in the table below.

#### Comparative example 10

55 500 g of carrier were impregnated with 325 ml of an aqueous solution containing 142,9 g of molybdenum trioxide, 61,7 g of cobalt carbonate, 58 g of phosphoric acid (85%), and 27 g of nitric acid (65%). The composition and properties of the catalyst obtained after drying and calcination were as listed in the table below.

Comparative example 11

500 g of carrier were first impregnated with 325 ml of an aqueous solution containing 157,8 g of ammonium dimolybdate and 2,2 g of phosphoric acid (85%). The material obtained after drying and calcination (618 g) was impregnated with 325 ml of an aqueous solution containing 126,6 g of cobalt nitrate.6H<sub>2</sub>O. The composition and properties of the catalyst obtained after drying and calcination were as listed in the table below. The two impregnating solutions used in this example were prepared by simply dissolving the components in question in water.

Example 12

The catalysts were compared with each other with respect to their desulphurization capacity. The techniques and equipment used in this process have been described in detail in Applied Catalysis 43, pp. 239 ff (1988); Ind. Eng. Chem. Process Des. Dev. 20, pp. 40 ff (1981); and Proc. 6th Int. Congr. Catal. 2, London 1976 (eds. G.C. Bond et al.), paper B34. The procedure was as follows.

Use was made of a Kuwait Straight Run Gas Oil having the following specification:

density at 50°C :	0,8145 g/ml
sulphur content :	1,175 wt.% (S)
nitrogen content :	92 ppm (N)

ASTM D86 distillation data:

IBP:	177°C
50 vol.% :	288°C
FBP :	365°C

The catalyst was charged to a reactor and first sulphided. To this end the gas oil, into which 2,5 wt.% of dimethyl disulphide (spiking agent) had been incorporated, was passed through the catalyst bed for 3 hours at a temperature of 100°C, a pressure of 30 bar (no H<sub>2</sub> flow), and an LHSV of 4,0 hr<sup>-1</sup> (prewetting), after which over a period of 8 hours the temperature was gradually increased to 320°C. During this increase in temperature the LHSV was 1,0 hr<sup>-1</sup>, the pressure continued to be 30 bar, and an H<sub>2</sub> flow was started up: H<sub>2</sub>/oil ratio 120 NI/l. The situation at 320°C was maintained for 10 hours, after which the sulphidation process was completed. Next, the spiked gas oil was replaced with the gas oil itself and the following test conditions were successively laid down:

Test condition	LHSV hr <sup>-1</sup>	H <sub>2</sub> /Oil NI/l	Pressure bar	Temperature °C
1	3,00	120	30	335
2	2,00	120	30	335

After dissolved H<sub>2</sub>S and NH<sub>3</sub> had been removed from the product streams (passage of N<sub>2</sub>), the sulphur contents of the products were determined by means of X-ray fluorescence (XRF) in accordance with ASTM D2622.

The data obtained was used to calculate the relative volume activity (RVA), with test results obtained with the same volume of a commercially available HDS catalyst (KF-742® ex Akzo Chemicals; chemical composition: 15,0 wt.% of MoO<sub>3</sub>, 4,0 wt.% of CoO, alumina carrier; SA: 270 m<sup>2</sup>/g; PV(Hg): 0,52 ml/g; MPD: 8,0 nm) being employed as a reference. First, the reaction speed constant k was calculated:

# EP 0 469 675 B1

$$k = \frac{\text{LHSV}}{n-1} \times [(1/S_{\text{prod}})^{n-1} - (1/S_{\text{feed}})^{n-1}]$$

The reaction order  $n$  was determined by means of iteration,  $k$  having the same value under the two test conditions. In order to compensate for differences in  $n$  for the various catalysts the LHSV for 92% HDS conversion was calculated:

$$\text{LHSV}_{92} = k \times \frac{n-1}{(1/0,08S_{\text{feed}})^{n-1} - (1/S_{\text{feed}})^{n-1}}$$

$$\text{RVA} = \frac{\text{LHSV}_{92}}{\text{LHSV}_{92(\text{REF})}} \times 100$$

The results are listed in the table below. They show that the catalysts employed in the process according to the invention were substantially more active than the comparative catalysts.

Table

Example	Catalyst properties							RVA
	per 100 g of composition							
	MoO <sub>3</sub> mmole (wt.%)	CoO mmole (wt.%)	P <sub>2</sub> O <sub>5</sub> mmole (wt.%)	SA m <sup>2</sup> /g	PV ml/g	MPD nm	%PV > 20 nm <sub>D</sub>	
1	144 (20,8)	68 (5,1)	14 (2,0)	207	0,41	8,0	2,9	126
2	142 (20,5)	68 (5,1)	13 (1,9)	193	0,40	8,2	2,6	123
3	147 (21,2)	67 (5,0)	3,3 (0,47)	235	0,42	7,6	4,3	126
4	143 (20,6)	67 (5,0)	7 (1,0)	210	0,41	8,2	3,3	130
5	171 (24,6)	67 (5,0)	21 (3,0)	169	0,37	8,2	1,9	118
6*	124 (17,8)	65 (4,9)	13 (1,8)	206	0,43	8,0	3,0	99
7*	144 (20,7)	53 (4,0)	21 (3,0)	201	0,41	8,0	**	99
8*	212 (30,6)	68 (5,1)	15 (2,1)	143	0,31	7,6	3,3	97
9*	127 (18,3)	148 (11,1)	15 (2,1)	185	0,37	7,6	4,2	83
10*	144 (20,7)	68 (5,1)	33 (4,7)	193	0,39	7,4	**	103
11*	137 (19,7)	68 (5,1)	1,4 (0,2)	217	0,42	7,8	4,0	89

\* comparative example

\*\* not available

**Example 13**

This Example illustrates the effectiveness of the catalysts used in the process according to the invention in deep hydrodesulphurization. The catalyst of Example 2 was compared with the commercially available KF-742® HDS catalyst mentioned in Example 12. The test procedure was the same as that described in said Example 12, except for the feedstock and the test conditions. The feedstock was a partially desulphurized Kuwait Straight Run Gas Oil having a density at 50°C of 0,8081 and a sulphur content of 0,165 wt.%. The test conditions were as follows:

Test condition	LHSV hr <sup>-1</sup>	H <sub>2</sub> /Oil N/I	Pressure bar	Temperature °C
1	1,5	120	30	375
2	3,0	120	30	375

After dissolved H<sub>2</sub>S and NH<sub>3</sub> had been removed from the product streams, the sulphur contents of the products were determined by means of XRF in accordance with ASTM D2622.

The data obtained was used to calculate the relative volume activity (RVA) in the same manner as described in Example 12, albeit that to compensate for differences in  $n$  for the two catalysts the LHSV in this case was calculated at a constant conversion for 98% HDS. It was found that the RVA, being equal to

$$\frac{\text{LHSV}_{98}}{\text{LHSV}_{98(\text{ref})}} \times 100,$$

was 161.

**Claims**

1. A process for the catalytic hydrodesulphurization of a hydrocarbon-containing feed having a metals content of Ni plus V not exceeding 15 ppm and a boiling point range at which more than 50 volume per cent of the feed boils below 600 °C, comprising contacting said feed under hydrodesulphurization conditions with a catalyst composition containing a porous, inorganic oxide carrier comprising transition alumina, a phosphorus component, a cobalt component, and a Group VIB metal component, wherein the phosphorus component content, calculated as P<sub>2</sub>O<sub>5</sub>, is 2 - 28 mmoles, the cobalt component, calculated as CoO, is 60 - 133 mmoles, and the Group VIB metal component content, calculated as trioxide, is 132 - 208 mmoles, all calculated on the basis of 100 grams of said catalyst composition, and said catalyst composition is prepared by a process in which a chemical precursor of the transition alumina is shaped, the shaped material is subjected to at least one calcining step in order to form transition alumina, and the precursors of the phosphorus component and the metal components are deposited on the carrier material prior to, during and/or after the shaping step, with the proviso that the cobalt component precursor is deposited after forming of the transition alumina.
2. A process according to claim 1, characterized in that said catalyst composition has a specific surface area of at least about 100 m<sup>2</sup>/g and a pore volume in the range of from about 0,25 to about 1,3 ml/g.
3. A process according to claim 2, characterized in that less than 5 percent of said catalyst's pore volume is in pores having a diameter of greater than 25 nm.
4. A process according to any one of claims 1-3, characterized in that the Group VIB metal is molybdenum.
5. A process according to claim 4, characterized in that said catalyst composition contains from 19 to about 23 weight percent molybdenum, from 4,5 to about 6 weight percent cobalt, and from 0,3 to about 3 weight percent phosphorus.
6. A process according to any one of claims 1 to 5, characterized in that the median pore diameter of said catalyst composition has a value in the range of from about 5 to 15 nm.



## Patentansprüche

1. Verfahren zur katalytischen Hydrierdesulfurierung einer Kohlenwasserstoffe enthaltenden Speisung mit einem Metallgehalt von Ni plus V von nicht über 15 ppm und einem Siedebereich, bei welchem mehr als 50 Volumen% der Speisung unter 600°C siedet, unter kontaktieren der Speisung unter Hydrierdesulfurierungsbedingungen mit einer Katalysatorzusammensetzung, die einen porösen, anorganischen Oxidträger enthält, der Übergangsaluminiumoxid, eine Phosphorkomponente, eine Cobaltkomponente, eine Komponente aus einem Metall der Gruppe VIB, wobei der als  $P_2O_5$  berechnete Phosphorkomponentengehalt 2-28 mMol beträgt, die als CoO berechnete Cobaltkomponente 60-133 mMol beträgt und der als Trioxid berechnete Gehalt an Metallkomponente der Gruppe VIB 132-208 mMol beträgt, wobei alles auf Basis von 100 g der Katalysatorzusammensetzung berechnet ist und die Katalysatorzusammensetzung nach einem Verfahren hergestellt wird, in welchem ein chemischer Präkursor des Übergangsaluminiumoxides geformt wird, das geformte Material mindestens einem Calcinierschritt zur Bildung des Übergangsaluminiumoxides unterzogen wird und die Präkursoren der Phosphorkomponente und der Metallkomponenten vor, während und/oder nach dem Formgebungsschritt auf dem Trägermaterial abgelagert werden, mit der Massgabe, dass der Präkursor der Cobaltkomponente nach Bildung des Übergangsaluminiumoxides abgelagert wird.
2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, dass die Katalysatorzusammensetzung eine spezifische Oberfläche von mindestens etwa 100 m<sup>2</sup>/g und ein Porenvolumen im Bereich von etwa 0.25 bis etwa 1.3 ml/g hat.
3. Verfahren nach Anspruch 2, dadurch gekennzeichnet, dass weniger als 5% des Porenvolumens des Katalysators in Poren mit einem Durchmesser von grösser als 25 nm vorliegt.
4. Verfahren nach einem der Ansprüche 1-3, dadurch gekennzeichnet, dass das Metall der Gruppe VIB Molybdän ist.
5. Verfahren nach Anspruch 4, dadurch gekennzeichnet, dass die Katalysatorzusammensetzung 19 bis etwa 23 Gew.% Molybdän, 4,5 bis etwa 6 Gew.% Cobalt und 0,3 bis etwa 3 Gew.% Phosphor enthält.
6. Verfahren nach einem der Ansprüche 1-5, dadurch gekennzeichnet, dass der mittlere Porendurchmesser der Katalysatorzusammensetzung einen Wert im Bereich von etwa 5 bis 15 nm hat.

## Revendications

1. Procédé d'hydrodésulfuration catalytique d'une charge contenant des hydrocarbures ayant une teneur en métaux de Ni plus V ne dépassant pas 15 ppm et une gamme de points d'ébullition telle que plus de 50% en volume de la charge ont un point d'ébullition inférieur à 600°C, comprenant la mise en contact de cette charge dans des conditions d'hydrodésulfuration avec une composition catalytique contenant un support poreux à base d'oxydes inorganiques comprenant une alumine de transition, un composant phosphoré, un composant de cobalt et un composant métallique du groupe VIB, où la teneur en composant phosphoré, exprimée en  $P_2O_5$ , est de 2 à 28 mmoles, la teneur en composant de cobalt, exprimée en CoO, est de 60 à 133 mmoles, et la teneur en composant métallique du groupe VIB, exprimée en trioxyde, est de 132 à 208 mmoles, toutes ces teneurs étant calculées sur la base de 100 grammes de cette composition catalytique, et cette composition catalytique est préparée par un procédé dans lequel un précurseur chimique de l'alumine de transition est façonné, le matériau façonné est soumis à au moins une étape de calcination pour former une alumine de transition, et les précurseurs du composant phosphoré et des composants métalliques sont déposés sur le matériau de support avant, pendant et/ou après l'étape de façonnage, à condition que le précurseur du composant cobalt soit déposé après la formation de l'alumine de transition.
2. Procédé selon la revendication 1, caractérisé en ce que cette composition catalytique a une surface spécifique d'au moins environ 100 m<sup>2</sup>/g (méthode BET) et un volume de pores dans la gamme de 0,25 environ à 1,3 ml/g environ.
3. Procédé selon la revendication 2, caractérisé en ce que moins de 5% du volume de pores de ce catalyseur sont constitués de pores ayant un diamètre supérieur à 25 nm.
4. Procédé selon l'une quelconque des revendications 1 à 3, caractérisé en ce que le métal du groupe VIB est le molybdène.
5. Procédé selon la revendication 4, caractérisé en ce que cette composition catalytique contient de 19 à environ 23% en poids de molybdène, de 4,5 à environ 6% en poids de cobalt et de 0,3 à environ 3% en poids de phosphore.

## EP 0 469 675 B1

6. Procédé suivant l'une quelconque des revendications 1 à 5, caractérisé en ce que le diamètre de pore médian de cette composition catalytique a une valeur comprise entre environ 5 et 15 nm.

5

10

15

20

25

30

35

40

45

50

55